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A STUDY OF POLYMERS
CONTAINING SILICON-NITROGEN BONDS

Progress Report 34 for the Period
November 4, 1963 to December 3, 1963

To

GEORGE C. MARSHALL SPACE FLIGHT CENTER
National Aeronautics and Space Administration
Huntsville, Alabama

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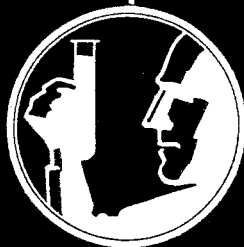
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ABSTRACT

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Aluminum ethoxide was found to catalyze the polymerization of bis(methylamino)diphenylsilane. The mechanism of polymerization is not understood, but it appears that the silicon-nitrogen bond is weakened by the presence of the aluminum compound with resulting condensation by elimination of methylamine.

A silylamine made from methylphenyldichlorosilane and methylamine reacted with dihydroxybenzenes to form polymers that were flexible and had good thermal stability. It will be necessary to improve the molecular weights to obtain better strength, but the reaction looks promising. This is the same reaction that has been used previously at George C. Marshall Space Flight Center with dianilinodiphenylsilane. Silylamines did not react satisfactorily with difunctional aromatic amines.

Attempts to induce ethoxysilanes to react with silylamines were not successful. Ammonium chloride and diphenyldichlorosilane were tried as catalysts, but polymers were not produced.

Silicon-nitrogen polymers with phenylene groups in the chain were studied further. The methyl-substituted compounds appeared to be the more useful, because they were tougher and more flexible than the phenyl-substituted compounds.

AUTHOR

A STUDY OF POLYMERS CONTAINING SILICON-NITROGEN BONDS

I. INTRODUCTION

Silicon-nitrogen compounds are being studied in an effort to produce thermally-stable materials that will be useful in the space program. This report covers the eighth month of the fourth year of the program.

Polymeric materials of principal interest at present are those made from 1,4-bis(dimethylchlorosilyl)benzene and methylphenyldichlorosilane. Each of these has been used to make polymers of attractive toughness and flexibility. Additional efforts are being made to improve the purity of reactants, as a possible way to obtain higher molecular weights and better strength.

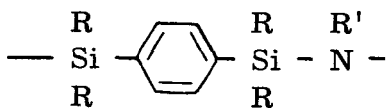
It was found that aluminum ethoxide either enhanced the polymerization of bis(methylamino)diphenylsilane or polymerized with it. One of the two main volatile products was methylamine, and the other was benzene. Brittle solid polymers that were not sensitive to atmospheric moisture were obtained.

Investigation is being continued in each of the areas mentioned.

II. SILICON-NITROGEN POLYMERS CONTAINING AROMATIC BRIDGES

A. Discussion

Polymers are being prepared from 1,4-bis(dimethylchlorosilyl)benzene and 1,4-bis(diphenylchlorosilyl)benzene by treating them first with methylamine or ammonia and subsequently polymerizing the derivatives by heating. The derivatives that have been made are represented by the following formula:



R = methyl or phenyl

R' = methyl or hydrogen

The polymers made from materials in which R was phenyl and R' was either methyl or hydrogen were invariably hard and brittle. They seem relatively less promising, because of brittleness, than the polymers made from materials in which R was methyl and R' was either hydrogen or methyl. Previous reports have described the initial experiments. In the past month attempts have been made to improve the polymers by prolonged heating in air or nitrogen and by heating in a closed vessel with air and oxygen, but no significant improvements over the initial results have been made.

The material in which R and R' were methyl was used to impregnate glass cloth to form a flexible material that may be useful for gaskets. Four layers of glass cloth were superimposed, impregnated with the liquid, and cured 24 hours at 190°C and 1 hour at 250°C. The product was tan in color. It appeared to be between Viton A and Teflon in both compressibility and thermal stability. As mentioned previously the polymer becomes elastic after heating for a few minutes at 100°C, then it hardens slowly after it returns to room temperature. If it is used as a gasket material, it may be desirable to heat the gaskets to 100°C before placing them in position.

The material in which R was methyl and R' was hydrogen was a fairly tough, white solid after being heated overnight at 250°C while nitrogen was bubbled through it. Attempts are presently being made to polymerize it further by prolonged heating in nitrogen at 250°C. The melt has become increasingly viscous with only slight darkening, but a solid has not yet been produced. Samples of the melt, when cured in thin films on aluminum panels, appear to have good stability, adhesion, and flexibility.

B. Experimental Details

1. Polymerization of the compound having R = methyl and R' = hydrogen

The white, waxy solid that was obtained from the reaction of 1,4-bis(dimethylchlorosilyl)benzene with ammonia was placed in a Teflon beaker and heated overnight at 250°C in a nitrogen atmosphere. The product was a thin liquid at 250°C and a viscous stringy liquid at room temperature, but it became brittle and cracked when heated at 450-500°C on an aluminum panel.

The white, waxy solid was placed in a 10-mm Pyrex test tube and heated at 250°C overnight while nitrogen was bubbled slowly through the melt for 18 hours. The cooled product was an opaque, white, tough solid that softened at 185-190°C. This solid was heated in a layer about 1 mm deep in a Teflon mold at 350°C for 2 hours in air. The product was a transparent, rubbery film at 250°C. At room temperature it was a brown, transparent, flexible solid that could be torn easily.

Attempts are now being made to polymerize the white, waxy solid by longer heating in nitrogen at 250°C. Preliminary evaluation of coatings made by heating small samples on aluminum panels at 450-500°C indicated good stability and flexibility, but a more extensive evaluation will be required to compare the material with coating agents made previously.

2. Polymerization of the compound having R- methyl and R'- methyl

The compound prepared from the reaction of 1,4-bis(dimethylchlorosilyl)benzene with methylamine was a viscous, tan liquid. Report 32, page 25, described its conversion to a tough tan solid by heating at 250°C in air. Attempts to polymerize it by heating in nitrogen apparently have been unsuccessful because the material has remained liquid.

The initial reaction product (the viscous, tan liquid) was heated in a 43-ml stainless steel bomb in air at 190°C for 40 hours. The product was a viscous, clear, brown liquid. Further heating in air, as in the previous reaction, resulted in formation of a brittle solid. With oxygen in the bomb a friable, brown, waxy solid was produced that formed good coatings on aluminum. It is being investigated further.

The initial reaction product was used to impregnate two samples of four superimposed layers of glass cloth in a shallow Teflon mold. The impregnated cloth was then heated at 190°C for 24 hours. The sheet was turned over several times during the first 8 hours of the curing period. At the end of 24 hours the mat was tacky at room temperature. Heating for 1 hour at 250°C eliminated the tackiness and produced the material described earlier in this section.

3. Polymerization of the compounds having R = phenyl and R' = methyl or hydrogen

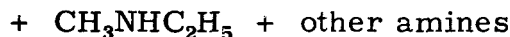
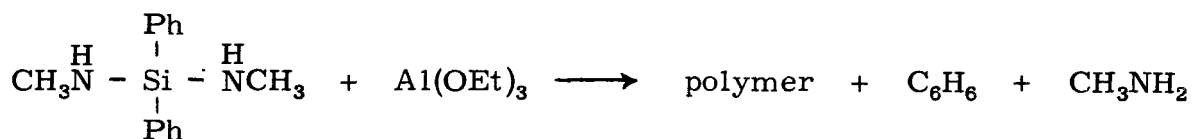
Reactions of 1,4-bis(diphenylchlorosilyl)benzene with ammonia and methylamine were previously described in Report 32, page 26. Attempts to carry out the polymerization in air at 250°C resulted in brown solids that were soft at 250°C and brittle at room temperature. More recently, attempts to carry out polymerizations in nitrogen at 250°C for 18 hours in Teflon beakers resulted in products that were thin liquids at 250°C and brittle solids at room temperature.

III. THE INFLUENCE OF ALUMINUM ETHOXIDE ON THE POLYMERIZATION OF BIS(METHYLAMINO)DIPHENYLSILANE

A. Discussion

Aluminum ethoxide apparently catalyzes some polymerization reactions of silylamines; but the reaction is complex, and it is not yet known whether aluminum ethoxide is a catalyst, a reactant, or both.

The following reaction occurred at 300°C:



So far, the polymers obtained have all been brittle, soluble solids. When the reactants were held long enough at 300°C, the product was infusible although it was soluble in benzene and other organic solvents. The products underwent no visible change on standing for several weeks in air, and they hydrolyzed so slowly in dilute acid that it was not practical to determine a neutral equivalent. The thermal stability of the products appeared to be good in that they did not undergo gross visible chemical decomposition at 400-500°C, but they cracked badly. Evidently the products all had low molecular weights. Furthermore, the aluminum ethoxide, or products derived from it, remained in the polymer matrix and may have continued to catalyze further reaction, thereby preventing attainment of a stable state.

Studies of the reaction mechanism are in progress. A complex mixture of volatile products is formed during polymerization. Benzene was 32% of the product, and the remainder consisted largely of 6 different amines. The elemental analysis indicated that more than half of the nitrogen was lost during polymerization.

The experiments already discussed were performed with stoichiometric quantities of aluminum ethoxide (3 equivalents per mole) and bis(methylamino)diphenylsilane (2 equivalents per mole). Polymerization also occurred when 10% or 1% of the equivalent quantity of aluminum ethoxide was used, but the reaction rates were slower.

B. Experimental Details

1. Equivalent quantities of aluminum ethoxide and bis(methylamino)-diphenylsilane

In the first reaction, equivalent quantities of aluminum ethoxide (2.24 g, 0.0138 mole) and bis(methylamino)diphenylsilane (4.99 g, 0.0206 mole) were placed in a 25-ml, 3-neck, round-bottom flask fitted with a reflux condenser and a thermometer. The mixture was heated until it began to evolve gas at about 200°C, even though the boiling point of bis(methylamino)diphenylsilane is about 350°C (judging from its boiling point at 1 mm). The odor of amine was strong. The evolution of gas

became slower as the temperature rose to 260°C in 1.5 hour, and a low-boiling liquid began to reflux. At the end of 2 hours, the vapors were drawn off by inserting a tube from an aspirator. The appearance of the bubbles in the melt indicated that the viscosity was high, and so the reaction was stopped. As the melt cooled and solidified, bubbles were entrapped to form a yellow, foamed mass. The solid portion was clear when viewed under a microscope. The mass was soluble in benzene, acetone, and chloroform but insoluble in carbon tetrachloride. After remaining at room temperature for 30 minutes it could not be remelted. A solution of the polymer in benzene dried on a watch glass formed a hard, brittle, crazed film. It did not lose its transparency while exposed to the laboratory air for two days. Another sample was examined periodically under a microscope for a week, and no evidence of evaporation or attack by moisture was seen.

A second reaction was run to obtain a product for analysis. Air was excluded by blowing the volatile liquid product away periodically with a nitrogen stream. Polymerization was stopped before the infusible state was reached. The product was pale yellow, brittle, and vitreous. Elemental analysis gave the following results:

Found: C, 58.19%; H, 5.96%; N, 3.0%

Calculated for total reactants: C, 59.37%; H, 8.22%; N, 6.96%
Al, 6.65%; O, 11.84%; Si, 6.96%

In an attempt to determine whether aluminum ethoxide was present in an uncombined state, the polymer was dissolved in acetone. It dissolved readily whereas aluminum ethoxide dissolves in acetone only very slowly. When water was added to the acetone solution of the polymer, a precipitate formed that did not have the appearance of an aluminum hydroxide floc. Furthermore, the precipitate was soluble in an excess of acetone, and so it appeared that the aluminum had become part of the polymer.

In an attempt to determine its neutral equivalent, a sample of the polymer was dissolved in acetone, and water was added until the precipitate just barely redissolved on stirring. Then 0.1 N acid was added. The needle of the meter used to determine the pH drifted badly, and it was finally decided that hydrolysis was too slow for determination of the neutral equivalent by this method.

A third reaction was run for the primary purpose of trapping and identifying the volatile products. It was run in a distillation apparatus with a receiver cooled by dry ice. Aluminum ethoxide, 2.2162 g (0.0137 mole) and bis(methylamino)diphenylsilane, 4.7558 g (0.0197 mole) were heated in a 25-ml distilling flask until gas was evolved. The distillate and evolved gas were passed into a condenser-receiver combination cooled by dry ice. After 3.5 hours of gentle boiling, a slow nitrogen stream was introduced to sweep the volatile product into the receiver. After 0.75 hour of additional heating the melt became viscous and solidified while foaming. The weight of solid product was 3.8839 g (55.7% of the starting material). The distillate weighed approximately 2.2168 g (31.8% of the starting material). In addition there was 0.0301 g (0.4%) of a high-boiling liquid in the tube between the still and the condenser-receiver. The total material accounted for was 88% of the starting material. The uncondensed gas was basic in character. However, the chromatographic results described below suggest that hydrocarbons may have been a large part of the uncondensed product.

Gas chromatography of the condensed product revealed that at least 10 compounds were present as shown in Table I. Six were basic and four were not. Methylamine (40%) and benzene (32%) were major components. The identification of methylethylamine and xylene suggested that disproportionation was extensive. The absence of large amounts of ethanol in the product was interesting. It is possible that ethanol may be produced but that it reacts as soon as it is formed to break a silicon-nitrogen bond. In that case it may be a chain stopper.

A similar reaction was run in tetralin which was chosen as a high-boiling inert solvent. Equivalent quantities of aluminum ethoxide and bis(methylamino)diphenylsilane, 7.23 g total, were dissolved in 25 ml of dry tetralin and refluxed for 12.5 hours. The tetralin was distilled off at reduced pressure, and the residue was a brown cloudy liquid. It was only partially soluble in benzene and acetone. Centrifugation of the benzene solution separated a gel-like mass. The clear benzene solution was evaporated in a stream of nitrogen, and another gel was obtained. Evidently the reaction in the solvent was different from the reaction without solvent, but no advantage was apparent.

Table I. Gas Chromatography of Product from Reaction of Aluminum Ethoxide and Bis(methylamino)diphenylsilane

<u>Fraction</u>	<u>T_R^a</u>	<u>Area %^b</u>	<u>Tentative identification^c</u>
1	0.1	trace ^d	
2	0.2	1 ^d	
3	0.3	2	tetramethylsilane
4	0.4	1 ^d	
5	0.6	5 ^d	
6	0.8	40 ^d	methylamine
7	1.0	32	benzene
8	1.7	15 ^d	methylethylamine
9	2.6	4	xylene
10	10.0	1	ethanol

^a Retention time, relative to benzene = 1.

^b Area % is essentially the same as mole percent.

^c The tetramethylsilane is questionable; the others are reliable.

^d These were found to be basic compounds as determined by disappearance when the sample was acidified.

The products of the reaction between aluminum ethoxide and bis-(methylamino)diphenylsilane were tried as coating agents, but they were not promising. When thin films were heated on aluminum panels at 300°C for 16 hours they flaked off or were easily scratched off with a fingernail.

2. Reaction with 10% of the equivalent quantity of aluminum ethoxide

In an attempt to determine whether the role of aluminum ethoxide was catalytic in the reaction with bis(methylamino)diphenylsilane, a reaction was run with 10% of the stoichiometric amount. In a 25-ml, 3-neck flask were placed 4.99 g (0.0206 mole) of bis(methylamino)diphenylsilane and 0.22 g (0.0014 mole) of aluminum ethoxide. The mixture was heated until gas evolution started. After 1.75 hours of heating, condensate began to form in the condenser. When sputtering became excessive as the condensate fell into the melt, nitrogen was used to blow the condensate out. At the end of 3 hours, total, the reaction was stopped. The product was a pale yellow, brittle, vitreous solid that softened in a capillary tube at 67-71°C. On the next day, heating was resumed for 6.5 additional hours. The softening point of the solid product, 3.3 g, was 114-122°C. Analysis for carbon and hydrogen gave the following:

Found: C, 65.74%; H, 5.50%; N, 7.39%; Al, 2.8%;
Si, 13.4%; remainder, 5.17%.

Calculated for total reactants: C, 67.77%; H, 7.60%;
N, 10.87%; Al, 1.04%; O, 1.85%; Si, 10.87%

Nuclear magnetic resonance spectra indicated that the ratio of phenyl to methyl groups was 1.5 : 1. No ethyl and no NH groups could be detected.

For the sake of comparison, bis(methylamino)diphenylsilane, alone, was boiled gently for 3 hours. Gas evolution was comparatively slow throughout the reaction. When cool, the product was a mixture of solid and crystalline material. There seemed to be no doubt that the aluminum ethoxide was accelerating the reaction.

A similar reaction was performed in a long open-end glass tube in an oven at 300°C for 22 hours. The product was a brown polymer that softened at 82-98°C. It appeared to be similar to the other polymers of this type in brittleness, solubility, and softening and so no further work was done on it.

3. Reaction with 1% of the equivalent quantity of aluminum ethoxide

The aluminum ethoxide-bis(methylamino)diphenylsilane reaction was run with only 1% of the stoichiometric amount of aluminum ethoxide. After 4.75 hours of heating at a temperature adjusted to keep gas evolving slowly (257-346°C as the reaction progressed) a viscous liquid was produced. The liquid solidified on cooling; the softening point was 97-117°C. The product resembled the others obtained from reactions with larger amounts of aluminum ethoxide in solubility and behavior on heating.

4. Attempted reactions with ethanol and phenol

To check the possibility that ethanol might be produced and have catalytic action in the reaction of aluminum ethoxide with bis(methylamino)-diphenylsilane, reactions were run with ethanol and phenol in 10% of the stoichiometric quantities. After being refluxed for 3 hours and left overnight at room temperature no solid product was obtained from either reaction. The phenol and ethanol reactions did not resemble any of the aluminum ethoxide reactions closely nor were they entirely like that with simple heating of bis(methylamino)diphenylsilane. It is clear that the aluminum ethoxide reaction is not simply a matter of forming ethanol by hydrogen exchange, followed by attack of ethanol on silicon-nitrogen bonds.

IV. REACTION OF DIAMINO SILANES WITH DIFUNCTIONAL AMINES AND PHENOLS

A. Discussion

It has been shown at the George C. Marshall Space Flight Center that diaminosilanes react with dihydroxybenzenes to form tough polymers with excellent thermal stability. Similar reactions have been tried here with diaminomethylphenyl silanes. It was postulated that the methyl group attached to the silicon would enhance the flexibility of the polymers. In addition, attempts were made to bring about the corresponding reaction of diaminosilanes with diaminobenzenes instead of dihydroxybenzenes.

1. Reactions of "methylphenyl methylamino silazane"

Methylphenyl methylamino silazane is used here to designate the product from the reaction of methylphenyldichlorosilane and methylamine (Report 33, pages 8 and 9). The methylphenyl methylamino silazane reacted rapidly with hydroquinone and p,p'-biphenol (4,4'-dihydroxybiphenyl) when no solvent was used. Reaction took place more slowly in solvent. With hydroquinone a black, tough, flexible, elastic polymer was obtained that hardened on prolonged heating at 350°C. With biphenol a harder polymer was obtained. Attempts to form coatings on aluminum resulted, by reason of failure to adhere, in unsupported thin, clear films that had fair tensile strength. Initially the films were quite flexible and were not permanently creased when folded, but they became extremely brittle when heated at 370°C for 16 hours.

Benzidine (4,4'-diaminobiphenyl) and p-phenylenediamine reacted slowly with methylphenyl methylamino silazane; the products were hard and brittle. Evidently, the molecular weights were too low for useful polymers.

2. Reaction of "methylphenyl anilino silazane"

The methylphenyl anilino silazane used in these trials was probably crude dianilinomethylphenylsilane. It reacted slowly with benzidine, and the product was a soft solid at room temperature. Attempts to cure the product further by heating in thin films caused much of it to evaporate. Apparently, polymerization occurred too slowly for any useful products to be formed.

Polymerization of the methylphenyl anilino silazane was attempted by heating it with 10% of the stoichiometric amount of aluminum ethoxide. Some volatile material distilled off in 8-9 hours of heating at 190-230°C, and the remainder was a brittle solid at room temperature. Attempts to cure it further resulted only in further embrittlement.

B. Experimental Details

1. Reactions of the "methylphenyl methylamino silazane"

a. With hydroxybenzenes

The preparation of the methylphenyl methylamino silazane, which was probably largely bis(methylamino)methylphenylsilane, was described in Report 33, pages 8 and 9. As described in Report 33, page 10, it reacted readily with hydroquinone in tetrahydrofuran, and subsequent heating of the product for 18 hours at 190°C produced a tough, resilient polymer. A more recent preparation heated at 190°C for 48 hours resulted in a harder and less tough polymer that cracked when it was strongly flexed. The inclusion of ethylenediamine silazane, 10%, in one sample improved the flexibility but decreased the strength. Additional work will be done on this reaction in an attempt to improve the molecular weight and the strength.

The methylphenyl methylamino silazane was treated with p, p'-biphenol with and without tetrahydrofuran as a solvent. In a 25-ml, 3-neck flask, fitted with a magnetic stirrer, reflux condenser, and thermometer were placed 5.4 g (0.03 mole) of the methylphenyl methylamino silazane, which was a liquid, and 5.5 g (0.03 mole) of p, p'-biphenol (4, 4'-dihydroxybiphenyl). A vigorous reaction occurred with foaming. The resulting viscous mass was heated at 235-270°C for 3.5 hours. When the product was hot, it was sticky and rubbery; when it cooled, it was hard and tough. The mass contained air and was not homogeneous, so an attempt was made to fuse it by heating 30 minutes at 350°C and 10 minutes at 400°C in a Teflon beaker. It did not fuse, but it did become tougher. The small disc, 8-mm thick and 20 mm in diameter could not be broken with the fingers, and vigorous pounding with a hard rubber mallet did not break it. A portion of the disc was dissolved in acetone, and the resulting solution was used to make a coating on aluminum. After 1 hour of heating at 185°C the coating appeared to be intact, but it could be peeled off with a knife blade. The freed film was transparent, flexible and fairly strong. A sample heated at 370°C for 16 hours became brittle.

In another preparation, the methylphenyl methylamino silazane, 5.4 g (0.03 mole) in 20 ml of tetrahydrofuran was dropped into 5.5 g (0.03 mole) of p, p'-biphenol in 50 ml of tetrahydrofuran. Some amine was evolved, and the temperature rose 15°C. The solution was refluxed for 4 hours, then the solvent was distilled off, and the residue was heated at 270°C for 1.5 hour. The product was a sticky, tan solid that became hard and brittle on standing. When heated on an aluminum panel in an attempt to form a coating it flaked badly.

b. With diamines

Recrystallized benzidine, 5.5 g (0.03 mole), and the methylphenyl methylamino silazane, 5.4 g (0.03 mole), were mixed in 40 ml of tetrahydrofuran and refluxed for 20 hours. There was no evidence of reaction, such as darkening or an increase in viscosity. The amount of methylamine evolved was almost negligible.

The same quantities of the two materials were then mixed without solvent. On heating, methylamine was first evolved at 60°C; the mixture became viscous when it reached 130°C, and continued heating at 230°C for 3.5 hours was accompanied by darkening and a slow increase in viscosity. The product solidified to a brittle dark brown solid when it was cooled. Attempts to form coatings on aluminum produced shiny, jet-black, brittle films with poor adhesion. Heating for 64 hours at 185-190°C did not indicate any promising properties.

Attempts to produce polymers from *p*-phenylenediamine and the methylamino silazane gave results similar to those just described.

2. Reactions of the methylphenyl anilino silazane

Report 33, page 10, described the preparation of the impure aniline derivative of methylphenyldichlorosilane. The crude product was distilled at 190-195°C at 0.04 mm pressure. The pale yellow distillate crystallized and melted at 72-80°C. Two recrystallizations from Skellysolve B raised the melting point to 77-80°C, and two additional recrystallizations did not change it. The elemental composition was:

Found: C, 72.98%; H, 6.76%; N, 8.47%; Si, 10.2%;
Total, 98.41%

Calculated for dianilinomethylphenylsilane, $C_{19}H_{20}N_2Si$:
C, 74.95%; H, 6.62%; N, 9.20%; Si, 9.23%

NMR spectra indicated that the ratio of methyl:-NH:phenyl groups was 1:2:3, which agreed with theory. However, identification is not claimed because of the departure from the theoretical elemental analysis. Therefore, it is called the methylphenyl anilino silazane.

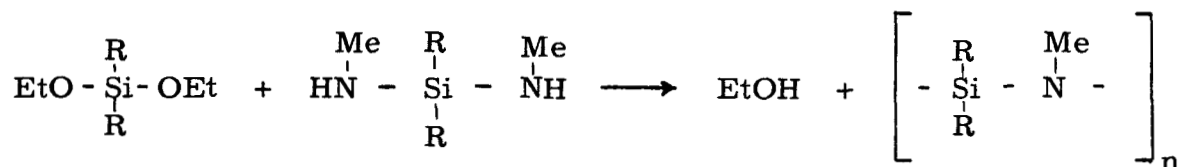
Equimolar quantities of benzidine and the methylphenyl anilino silazane were mixed in tetrahydrofuran and refluxed for 11 hours with no visible signs of reaction. The solvent was removed, and the reactants were heated at 205-210°C for 2 hours. A small amount of liquid, believed to be aniline, distilled at 175°C. The residue was a dark, sticky solid. Attempts to polymerize the solid further by heating it on a panel or in an open beaker at 185°C for 16 hours resulted largely in evaporation. The reaction was evidently too slow to be useful.

The methylphenyl anilino silazane, 5.0 g (0.018 mole), and aluminum ethoxide, 0.19 g (0.0012 mole) were heated at 190-195°C for 3 hours. The pressure was reduced by an aspirator, and an undetermined amount of volatile liquid was removed. Heating was continued at 220-230°C for 5 hours, and the pressure was reduced again to strip off the volatiles. The product was a brittle solid at room temperature. Attempts to make coatings of it or to decrease its brittleness by further polymerization were unsuccessful.

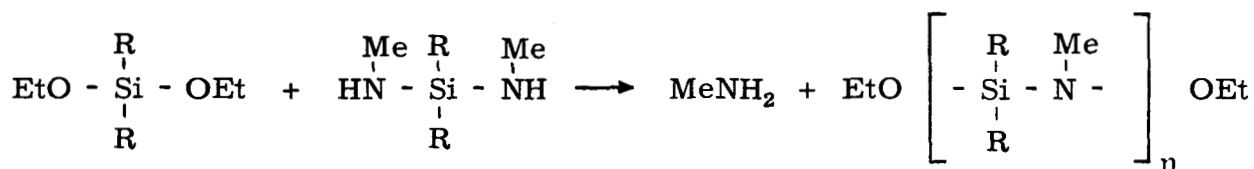
V. ATTEMPTS TO INDUCE A REACTION BETWEEN ETHOXYSILANES AND AMINOSILANES

A. Discussion

If ethoxysilanes and aminosilanes would react with the elimination of either an amine or an alcohol, a route would be open to polymers.



Any ethanol produced would be likely to react with Si-NHMe groups to release methylamine and produce a new Si-OEt group, which could then react with additional Si-NHMe groups. The net result would be this, with the ethoxy groups being required in relatively small amounts:



Bis(methylamino)diphenylsilane and dimethyldiethoxysilane were heated together under three different sets of conditions: the two alone, and the two with catalytic amounts of ammonium chloride and of diphenyldichlorosilane. There was no evidence that the two compounds reacted to form an appreciable amount of polymeric material. One reason may have been that the ethoxysilane boiled at 113°C and so high temperatures could not be used. Higher pressures and temperatures will be tried.

B. Experimental Details

Three attempts were made to cause reaction between bis(methylamino)diphenylsilane and dimethyldiethoxysilane. The two did not react when they were refluxed, and so ammonium chloride and diphenyldichlorosilane were tried as catalysts:

1. Without catalyst

Bis(methylamino)diphenylsilane (1.62 g, 0.007 mole) and dimethyldiethoxysilane (1.00 g, 0.007 mole) were refluxed for 10 hours. The temperature of the mixture rose gradually from 121-138°C. The product was a cloudy, viscous liquid. Evidently some polymerization occurred, but it could have been a result of self-condensation of bis(methylamino)diphenylsilane. Since a much higher degree of polymerization was required for the reaction to be useful, the two experiments below with acidic materials were tried.

2. With ammonium chloride

Bis(methylamino)diphenylsilane (10.0 g, 0.041 mole) and dimethyldiethoxysilane (6.08 g, 0.041 mole) were mixed and refluxed for 15.5 hours, and the product was still liquid. Then 0.34 g (0.006 mole) of ammonium chloride was added, and refluxing was continued. A strong odor of amine was noticed after the ammonium chloride was added. After 5 hours of refluxing with ammonium chloride, the reaction was terminated, and 4.0 g of volatile material was distilled off at atmospheric pressure. Its index of refraction, n_D^{26} 1.3790, was close to that of dimethyldiethoxysilane, n_D^{26} 1.3798, and different from that of ethyl alcohol, n_D^{26} 1.3590. The residue was a viscous liquid. Consequently, it was concluded that there had been little or no reaction.

3. With diphenyldichlorosilane

Bis(methylamino)diphenylsilane (5.0 g, 0.0206 mole), dimethyldiethoxysilane (3.04 g, 0.0206 mole), and diphenyldichlorosilane (0.16 g, 0.0006 mole) were refluxed for 9 hours. No evolution of gas or increase in viscosity was apparent. A small amount, 1.8 g, of volatile material was distilled off, and a soft solid residue was obtained. Again the amount of polymerization that occurred was insufficient to be of interest.

VI. ANTICIPATED WORK

The investigation of the role of aluminum ethoxide in polymerization of silylamines will be extended with analyses of the volatile products and attempts to use aluminum compounds for low-temperature curing. The activity of magnesium ethoxide will also be investigated.

Additional work will be done on the condensation polymerization of silylamines with difunctional phenolic compounds. Reactants will be purified in an effort to obtain higher molecular weights.

The study of triethylamine and other tertiary amines as retarders for cyclization in the reaction of chlorosilanes with amines will be continued.

A study of heats of combustion as indicators of aromaticity in cyclic silazanes will be started.

The preparation of the silicon-nitrogen polymers with phenylene bridges will be repeated with special efforts to achieve high purity and high molecular weights. Although much additional effort is considered to be warranted, only a small amount of additional work is planned because of the time allotment under the present contract.

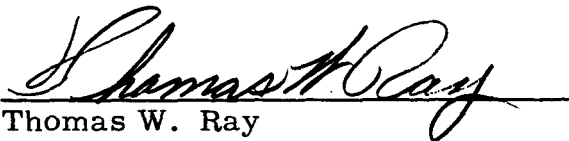
VII. TIME EXPENDITURE

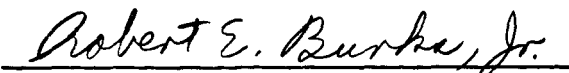
The time expenditure during the monthly period covered by this report was 619 man hours.

ACKNOWLEDGMENTS

Mr. Robert E. Lacey, Senior Chemical Engineer, has assisted with the planning and interpretation of the laboratory work. Miss Mary Ann Fromhold, Assistant Chemist and Mr. Charles L. Christy, Jr., Chemical Technician, assisted with the laboratory work.

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Birmingham, Alabama
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PROGRAM PLANNING CHART

	Allotted time, man-hours	1963												1964		
		April	May	June	July	August	September	October	November	December	January	February	March			
A. Synthesis of Polymers and Compounds with Desired Characteristics																
1. Lubricants - unsymmetrical derivatives of cyclic silazanes (see B. 1. b)	400			X	X											
2. Elastomers - silyl derivatives of ethylenediamine (see B. 7)	400															
3. Structural plastics	900	X	X	X	X	X										
B. Study of the Chemistry of Silicon-Nitrogen Compounds																
1. Metallation of silylamines as a method of synthesis	500	X	X	X	X											
a. Polymers	-															
b. Lubricants (see A. 1)	900							X	X	X	X					
c. Organometallics																
2. Polymerization of cyclic silazanes at high temperatures and pressures	280				X											
3. Condensation polymerization of silylamines with difunctional aromatic compounds	280							X	X	X						
4. Steric factors to inhibit cyclization	900							X	X	X						
5. Polyethylenimine as a source of silicon-nitrogen polymers	400							X	X	X						
6. Properties of methyldiamine silazanes	200															
7. Elastomers from ethylenediamine silazanes (see A. 2)	-															
8. Addition of silicon tetrafluoride to silazanes and amines	280															
9. Heats of combustion as indicators of aromaticity	420															
10. Polymers from methyltrichlorosilane and silicon tetrachloride	420															
11. Silicon-nitrogen compounds with aromatic bridges	510	X	X	X	X			X	X	X						
12. Factors affecting hydrolytic and thermal stabilities	510			continuous												
C. Evaluation of Polymers (thermal, hydrolytic, and radiation stability)	510															
D. Applications - Search for New Uses	510															
E. Heat Barriers	510															
F. Preparation of Final Report	170															
	9000															X

Descriptions correspond to sections of Proposal 2186 - March 20, 1963.